Pressure Volume Temperature (P-V-T) Relationships and Thermo elastic Properties of Geophysical Minerals

A PROPOSAL FOR

Ph.D PROGRAMME

BY

MONIKA PANWAR

UNDER THE SUPERVISION OF

DR SANJAY PANWAR
ASSISTANT PROFESSOR
DEPARTMENT OF PHYSICS
MAHARISHI MARKANDESHWAR UNIVERSITY, MULLANA
(AMBALA) - 133207

DR S K SRIVASTAVA
PROFESSOR
DEPTT OF ELEC & COMM ENGG
GEETA INSTITUTE OF MGMT & TECH
KANIPLA
(KURUKSHETRA) -136118

DEPARTMENT OF PHYSICS
MAHARISHI MARKANDESHWAR UNIVERSITY
MULLANA (AMBALA)-133207

APRIL 2010

1. Introduction

Geophysical minerals are the major constituents of the Earth's lower mantle and core such as $MgSiO_3$, MgO, Al_2O_3, CaO and Mg_2SiO_4. Periclase (MgO) is a simple oxide with cubic NaCl structure. Thermo elastic properties like thermal expansivity (α), isothermal bulk modules (K_T), volume expansion ratio of geophysical minerals such as MgO, CaO, Mg_2SiO_4, NaCl, KCl etc. under high temperature and high pressure has been studied by using parameter like Anderson-Gruneisen parameter (δ_T) and equations of states (EOS).

Elastic properties significantly influence fundamental properties of solids viz., interatomic potential, equations of state (EOS), specific heat, thermal expansion, Debye temperature, melting point and Gruneisen parameter via elastic constant. Values of elastic constant provide a valuable information about the bonding characteristics between adjusted atomic planes and anisotropic character of the bonding and structural ability. The analysis of temperature and pressure dependence of thermo-elastic and thermo-dynamic parameters is of great interest in studying the Earth's interior. Anharmonic effects in very high temperature region result in the deviation from the linearity of thermal pressure. Thermo elastic behavior of solids at high temperature gives the knowledge of temperature dependence of elastic modulii. Several empirical formulations have been developed to understand the change in elastic constants associated with variation temperature at atmospheric pressure.

Various isothermal equations of state (EOS) such as the Birch-Murnaghan EOS [1], the Vinet EOS [2], the Shanker EOS [3], and the logarithmic EOS [4] are used to study the pressure-volume relationships and the isothermal bulk modulus (K_T). The study of Anderson Gruneisen parameter not only provides information about interatomic forces but also predict the microscopic behavior of different thermodynamic properties. At high temperature, the extrapolation of thermal expansivity (α) is done on the basis of its non-linear model with change in temperature. Non-linear relationships for thermal expansivity (α) and isothermal bulk modulus (K_T) are the results of anharmonic effects in high temperature region, i.e. at temperature greater than Debye temperature (θ_D). At very high compression the thermal expansivity (α) is almost independent of temperature. The product of thermal expansivity and isothermal bulk modulus remains constant in high temperature region but such approximation does not hold well.

The Anderson-Gruneisen parameter (δ_T) is also useful for solving certain geophysical and astrophysical problems. Thermal expansivity is very important parameter to interpret the

thermodynamic and thermo elastic behavior of materials at high temperature and pressure because most of the errors in calculations of thermodynamic functions arise due to the uncertainty of thermal expansivity at high temperature and pressure. The temperature dependence of thermal expansivity (α) is extrapolated at high temperature region for NaCl, KCl, MgO and CaO which in turn predict the volume expansion ratio.

2. Literature Review

The equations of state (EOS) used in geophysics emerged with the studies of Love [5]. Keane [6] introduced K'_{∞} as a finite strain parameter. Stacey [7] developed a method for formulating equations based on the finite strain theory. Anderson [8] showed the variation of volume thermal expansion coefficient with specific volume. The isothermal derivative of the bulk modulus with pressure was evaluated at zero pressure. Isaak *et al.* [9] calculated the temperature and pressure dependence of the thermo elastic properties of MgO using potential-induced breathing model. Anderson *et al.* [10] evaluated the value of Anderson parameter (δ_T) for the lower mantle region of the Earth. It was asserted that $-(\partial ln\ \alpha / \partial ln\ \delta_T)$ must be between 4 and 6 in the lower mantle region of the Earth. The value of thermal expansivity (α) over a wide range of compression upto 0.6 was computed by Anderson *et al.* [11] in the range of room temperature to 2500K for MgO. They reported a simple relationship for volume dependence of thermal expansivity along an isotherm. The high temperature measurements of elastic constants and related temperature derivatives of geophysical minerals were reviewed and discussed by Anderson *et al.* [12]. A number of correlations between these parameters were also presented. The enthalpy at high pressure and the effect of pressure on the heat capacity of periclase (MgO) were determined by Xia and Xiao [13]. It was found that the enthalpy and heat capacity are linear with pressure at small compression. Using such linear relations for periclase (MgO) at small compression, a formula for thermal expansivity at high temperature and high pressure was presented according to the thermodynamic identities. Kumar [14] computed the coefficient of volume thermal expansion for NaCl from atmospheric pressure to the structural transition pressure and at the temperature ranging from room temperature to the melting temperature.

Wang and Reeber [15] reported the influence of thermal defects on high pressure thermal expansion. It is demonstrated that at lower mantle the thermal defects may be neglected. Anderson [16] compiled the experimental data for temperature dependence of thermodynamic quantities for many geophysical minerals at high temperature. Wang and

Reeber [17] derived an analytical expression for thermal defect contribution on thermal expansion coefficient. Thomas and Shanker [18] estimated the second order elastic constants such as C_{11}, C_{12}, C_{14} and isothermal bulk modulus K_T along with volume thermal expansion coefficient for NaC1 crystal in the temperature range 294K to 766K using Tallon's model [19] based on the concept of modified Anderson-Gruneisen parameters (δ_T).

Shanker and Kushwah [20] proposed a method to determine volume expansion with temperature along isobars for NaC1 crystal up to a pressure of 30 GPa and a temperature of 773 K; and for $MgSiO_3$ upto a pressure of 160 GPa and a temperature of 3000K. A simple theoretical method for the determination of bulk modulus and equation of state was proposed by Pal *et al*. [21] at different temperatures. Jacobs and Oonk [22] examined the relationships between thermal pressure and volume expansion ratio. Different thermo-elastic properties were calculated at high temperature for the solids, with the help of Birch [1] and Tallon's models [19]. Singh and Chauhan [23] analyzed the temperature dependence of thermal expansivity and isothermal bulk modulus in terms of the Anderson-Gruneisen parameter and thermal pressure. Singh *et al*. [24] analyzed a new relationship between thermal expansivity (α) and isothermal bulk modulus (K_T) for ionic solids such as NaC1, KC1, MgO and CaO. They observed a linear relationship between α and K_T, for a wide range of temperature at 1 bar pressure. Sushil *et al*. [25] reformulated the equations of state (EOS) for solids based on Lagrangian EOS and analyzed the finite-strain equations of state (EOS) under high pressures. Comparative study of Keane's [6] and Stacey's [7] equations of state (EOS) are examined by Shanker and Singh [26], which was based on the variation of K' with pressure and obtained the second volume derivative of the Gruneisen parameter γ for the lower mantle and the core of the Earth. Srivastava [27] analyzed a new elementary relationship among α, K_T and V_T/V_0 for ionic solids and concluded that the Anderson- Gruneisen parameter (δ_T) increases with temperature in very high temperature domain. The results are valuable to understand the thermodynamic and thermo elastic properties of solids at high temperature. At zero pressure the elastic constants, bulk modulus and Debye temperature decreased monotonically over the wide range of temperature (0-1100K) [28].

Vinod *et al*. [29] proposed the empirical relationships for temperature dependence of thermal pressure at atmospheric pressure for NaC1 and KC1 solids. It is found that the thermal pressure is a complex function of temperature and deviates from linearity in high-temperature region. The temperature dependence of volume expansion ratio is established

with the help of the thermal pressure. Srivastava [30] studied the thermo-elastic constant of ionic solids NaC1 and KC1 and the minerals MgO, CaO and Mg_2SiO_4 using the tabulated data complied by Anderson and Isaak [12]. Singh *et al.* [31] suggested a theory to describe the elastic behaviour of alkaline earth oxides under high pressure.

Shanker *et al*. [32] discussed the behaviour of solids in the limit of infinite pressure ($P\rightarrow\infty$) by using the relationships for the volume dependence of the Gruneisen parameter (γ). Xing *et al*. [33] observed a precise relationship showing exponential dependence of their elastic moduli on isobaric volume expansion for some typical solids such as NaC1, KC1, MgO and CaO at high temperatures. They calculated the value of elastic moduli at different temperatures. Srivastava *et al*. [34] found that the entropy of MgO decreases with increasing compression along an isotherm. They computed P-V-T relationships and compression dependence of isothermal bulk modulus with the help of Stacey's equation of state [7]. Fang [35] developed a simple and straight forward method for evaluating and predicting elastic moduli of MgO and CaO minerals at high temperatures based on the approximation, as suggested by Wang and Reeber [17]. Srivastava *et al*. [36] developed a model for compression dependence of thermal expansivity. With the help of this model they evaluated compression dependence of thermal expansivity for lower mantle of the Earth.

3. Proposed Work and Methodology

Temperature dependence of elastic constants is useful to investigate the thermo-elastic behaviour of solids at high temperature under isobaric conditions. Some empirical formulations have been developed to understand the change in elastic constants with change in temperature at atmospheric pressure. Although several researchers have studied various thermo-elastic properties using equation of state. Still, the pressure, volume, temperature (P-V-T) relationships and thermo-elastic properties of geophysical minerals have not been fully understood.

The present study will be based on high pressure thermodynamics applicable up to extreme pressure. The study will aim to develop new phenomenological, semi-phenomenological and empirical formulations to understand the behaviour of geophysical minerals in the region of interior of the Earth.

The present study shall consist the following:

1. The study of pressure, volume, temperature (P-V-T) relationships for geophysical minerals at high temperature and high pressure.
2. Thermal and elastic properties under extreme conditions.
3. The thermal expansivity of Geophysical minerals such as MgO, Mg_2SiO_4, $MgSiO_3$, Al_2O_3, $Mg_2Al_2O_4$.
4. The volume dependence of the Gruneisen ratio (γ) and thermal expansivity.

References

[1] F. Birch: J. Geophys. Res., **1952**, 57, p 227.

[2] P. Vinet, J. Ferrante, J.H. Rose and J.R. Smith: J. Geophys. Res., **1989,** 1, p 1941.

[3] J.P. Poirier and A. Tarantola: Phys. Earth Planet, **1998**, 109, p 1.

[4] J. Shanker, S.S. Kushwah and P. Kumar: Physica B. Condensed Matter, **1997**, 233(1), p 78.

[5] A.E.H. Love: A Treatise on the Mathematical Theory of Elasticity fourth edition, Cambridge University Press, Cambridge, **1927**.

[6] A. Keane: Aust. J. Phys., **1954**, 7, p 322.

[7] F.D. Stacey: Phys. Earth Planet Inter., **2001,** 12, p 179.

[8] O.L. Anderson: J. Geophys. Res., **1967,** 72, p 3661.

[9] D.G. Isaak, R.E. Cohen and M.J. Mehl: J. Geophys. Res., **1990**, 95.

[10] O.L. Anderson, A. Chopelas and R. Boehler: Geophys, Res. Lett., **1990,** 17, p 685.

[11] O.L. Anderson, H. Odd and D.G. Isaak: Geophys. Res. Lett., **1992**, 19**,** p 1987.

[12] O.L. Anderson, D.G. Isaak and H.Oda: Rev. Geophys, **1992,** 30**,** p 57.

[13] X-Xia and J. Xiao: J. Phys. Chem. Solid, **1993**, 54, p 629.

[14] M. Kumar: Sol. Stat. Comm., **1994**, 92, p 463.

[15] K. Wang and R.R. Reeber: Goopy. Res. Lett., **1995**, 22, p 1297.

[16] O.L. Anderson: Equations of State of Solids for Geophysics and Ceramic Sciences, Oxford University Press, New York, **1995**.

[17] K. Wang and R.R. Reeber: Phys. Chem. Minerals, **1996**, 23, p 354.

[18] L.M. Thomas and J. Shanker: Phys. Stat. Sol. (b), **1996**, 195, p 361.

[19] J.L. Tallon: J. Phys. Chem. Solids, **1980**, 41, p 837.

[20] J. Shanker and S.S. Kushwah: Physica B. Condensed Matter, **1998,** 254, p 45.

[21] V. Pal, M. Kumar and B.R.K. Gupta: Phys. Chem. Mineral, **1999**, 60(12), p 1895.

[22] M.H.G. Jacobs and H.A.J. Oonk: J. Phys. Chem. Phys, **2001**, 3, p 1394.

[23] K.S. Singh and R.S. Chauhan: Physica B. Condensed Matter, **2002,** 315 (1), p 74.

[24] B.P. Singh, S.K. Srivastava and K. Dinesh: Physica B. Condensed Matter, **2004**, 349, p 401.

[25] K. Sushil, K. Arunesh, P.K. Singh and B.S. Sharma: Physica B. Condensed Matter, **2004**, 352(1), p 134.

[26] J. Shanker and B.P. Singh: Physica B. Condensed Matter, **2005,** 370(1), p 78.

[27] S.K. Srivastava: Ind. J.Phys, **2005,** 79(66), p 607.

[28] X. Feng Li, X.R. Chem. and C.H. Meng: Sol. Stat Comm, **2006**, 139, p 197.

[29] K. Vinod, V.S. Malik, S.K. Sharma and S.K. Srivastava: J. Phys. Chem. Solids, **2007,** 68(1), p 32.

[30] S.K. Srivastava: J.Phys Chem. Solids, **2007,** 387 (1), p 396.

[31] S.P Singh, S. Gupta and S.C. Goyal: Physica B. Condensed Matter, **2007,** 307(2), p 307.

[32] J. Shanker, B.P. Singh and H.K. Baghel: Physica B. Condensed Matter, **2007,** 387(1), p 409.

[33] L.L. Xing, X.C. Peng and Z.H. Fang: Physica B. Condensed Matter, **2007,** 393, p 255.

[34] S.K. Srivastava, S.K. Sharma, K. Vinod and V.S. Malik: J. Phys. Chem. Solids, **2008,** 60(4), p 1029.

[35] Z.H. Fang: Solid State Sciences, **2008,** 10(7), p 950.

[36] S.K. Srivastava, P. Sinha, B.S. Kushwah: J. Phys. Chem. Solids, **2009,** 70(2), p 356.

[37] L. Burakovsky and D.L. Preston: J. Phys. Chem. Solids, **2004,** 65, p 1581.

[38] F.D. Stacey and P.M. Davis, Phys. Earth Planet Inter., **2004,** 142, p 137.